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ENERGY SHIFT OF ALKALI EARTHS IN THE VICINITY OF METAL SURFACES--ETC(U)

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Cs on W, and K and Cs on PrSb. Gadzuk's theory is reviewed and criticized for self-consistency.

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1. INTRODUCTION

In the theory of heterogeneous catalysis, it is generally assumed that the d electrons of transition metal catalysts are dominant in the desired chemical reaction taking place near the surface.¹ However, a microscopic mechanism describing how the d electrons in the surface states enter into the chemical reaction has not previously been proposed. Also, the f electrons are assumed responsible for the successful catalytic activity of compounds composed of rare-earth ions; a successful theory is lacking.

We have proposed² a concept describing how a rare-earth ion in the surface of a metal might enter into a reaction of an atom near the surface and increase the rate of ionization of the atom under certain favorable conditions. The concept is based upon an extension of a previous theory of the crystal field parameters, B_{nm} ,³ which explained the splitting of energy levels of rare-earth ions in bulk rare-earth monochalcogenides and monpnictides. That theory was based upon the use of the Thomas-Fermi model of electrons in a metal and a sum over the various constituent ions to obtain the lattice sum parameters, A_{nm} , and consequently the B_{nm} . Then the lattice sum was formed for an ion in the surface of the metal, and the B_{nm} for an ion in the surface were obtained. With these parameters, the energy levels and corresponding wave functions were obtained. These wave functions were used in a semiclassical approximation to calculate the charge density of the rare-earth ion and, consequently, the electric potential near the surface of the metal. This potential was shown to depend on the energy

¹J. C. Slater and K. H. Johnson, *Quantum Chemistry and Catalysis*, *Physics Today* (October 1974), 34.

²C. A. Morrison, N. Karayianis, and D. E. Wortman, *A Possible Use of the Surface States of Transition and Rare-Earth Metal Ions in the Theory of Catalysis*, *Harry Diamond Laboratories TR-1752* (April 1976).

³C. A. Morrison, *Phys. Lett.*, **51A** (1975), 49.

level of the rare-earth ion in the surface and also to depend on the crystallographic plane of the surface. This potential along with a calculation using standard metal-ion interactions was proposed to illustrate the utility of the theory. For those calculations, we chose two papers by Gadzuk,^{4,5} in which the ionization of alkali earths by W or Pt was calculated by using perturbation theory and metal-ion interactions obtained by using classical electrical image theory.

In this report, we investigate Gadzuk's theory for his examples and correct some apparently typographical errors in his papers. Then we extend his results to include the interactions created by the ionic nature of the atom in the surface of the metal. Finally, this calculation is done for the metal PrSb and the added interaction created because the rare-earth ion in the surface is in one of the low-lying surface energy levels.

2. GADZUK'S THEORY OF SURFACE INTERACTIONS

Gadzuk^{4,5} gave a theory of ad-atom-metal interactions, in which the ad-atom is assumed to interact with the metal according to classical image theory. Details of the calculation of the energy shift are given in appendix A. Here we state the underlying physical considerations and give the results for Cs adsorbed on W and K adsorbed on Pt, which Gadzuk considered.

2.1 Interactions of Atom and Solid

Consider the physical configuration and coordinate system shown in figure 1. The nucleus of the ad-atom is at the point (0,0,0);

⁴J. W. Gadzuk, *Surface Science*, 6 (1967), 133.

⁵J. W. Gadzuk, *Surface Science*, 6 (1967), 159.

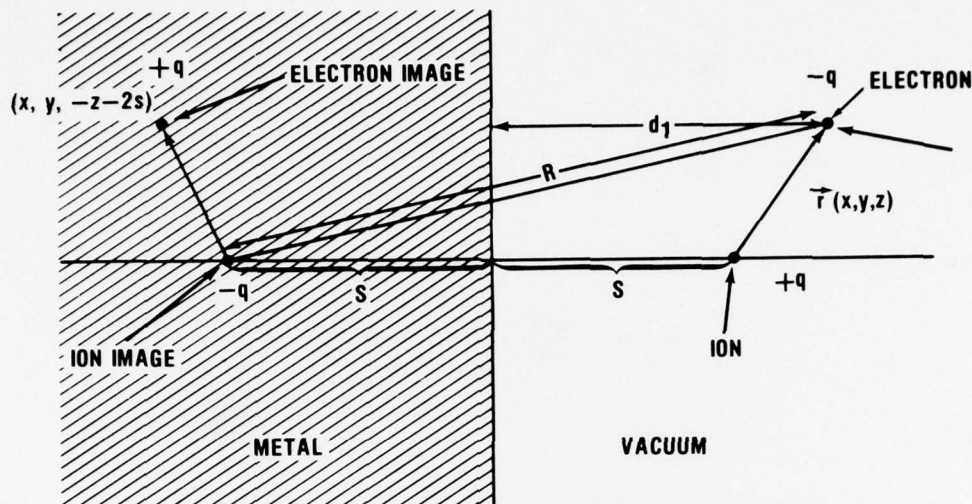


Figure 1. Physical configuration and coordinate system for alkali earth adsorption.

the electron is at $r = (x, y, z)$. The half space $z \leq -s$ is assumed to be occupied by metal. The interaction of the atom with the metal is represented by classical image theory which, for the electron on the alkali earth, is given by (app A)

$$V_i = -\frac{q^2}{4d_1} + \frac{q^2}{R} - \frac{q^2}{r}, \quad (1)$$

where

- V_i is the interaction energy,
- $q^2/4d_1$ is the interaction of the electron with its own image,
- q^2/R is the interaction between the electron and the ion image,
- q^2/r is the interaction of the electron with the ion core.

This last term is present even in the absence of the metal. Gadzuk thus chooses the single electron Hamiltonian, H , to be

$$H = - \frac{\hbar^2}{2m} \nabla^2 - V_0, \quad z < s_c - s, \quad (2)$$

$$H = - \frac{\hbar^2}{2m} \nabla^2 - \frac{q^2}{4d_1} + \frac{q^2}{R} - \frac{q^2}{r}, \quad z > s_c - s,$$

where s_c is chosen so that

$$-V_0 = - \frac{q^2}{4d_1} + \frac{q^2}{R}, \quad z = s_c - s, \quad (3)$$

where

\hbar is Planck's constant,

m is the electron mass,

∇^2 is the Laplacian operator,

V_0 is the sum of the Fermi energy, E_F , and the work function, ϕ ,

z is the coordinate normal to the metal surface,

s_c is the cutoff distance,

s is the distance of the nucleus from the surface.

If we assume that the coordinates x and y of the electron are small compared to s (the assumption made by Gadzuk) the value of s_c given by equation (3) is

$$s_c = \frac{1}{2} \left\{ [(s + \lambda)(s + 9\lambda)]^{1/2} - s - 6\lambda \right\}, \quad (4)$$

where $\lambda = q^2/4V_0$. If V_0 is given in electron volts, then $\lambda = 3.6/V_0$ in angstrom units. The variation of s_c with s is shown in figure 2 for Pt and figure 3 for W. (The curves labeled by ionic charge $Q_1 = 0$ are pertinent here.)

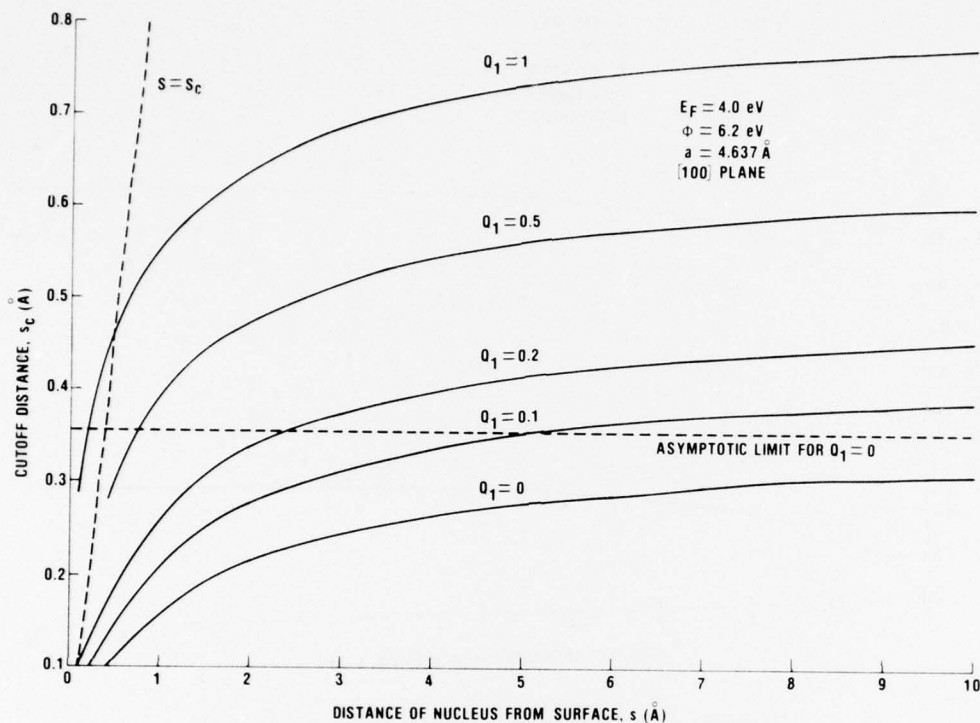


Figure 2. Cutoff parameter for platinum.

2.2 Energy Shift

In his theory of ionization of alkali earths, Gadzuk chose as wave functions of the electron the 2s hydrogenic type wave functions

$$\psi = N(1 - \alpha r) e^{-\alpha r} \quad (5)$$

with $\alpha = 0.99 \text{ \AA}^{-1}$ for Cs and $\alpha = 1.16 \text{ \AA}^{-1}$ for K. These values of α were chosen so that the hydrogenic wave functions closely approximated the exact self-consistent calculations of Herman and Skillman.⁶ The energy shift of the electron on the alkali atom is obtained by using first-order perturbation theory. That is,

⁶F. Herman and S. Skillman, *Atomic Structure Calculations*, Prentice Hall, Inc., Englewood Cliffs, NJ (1963).

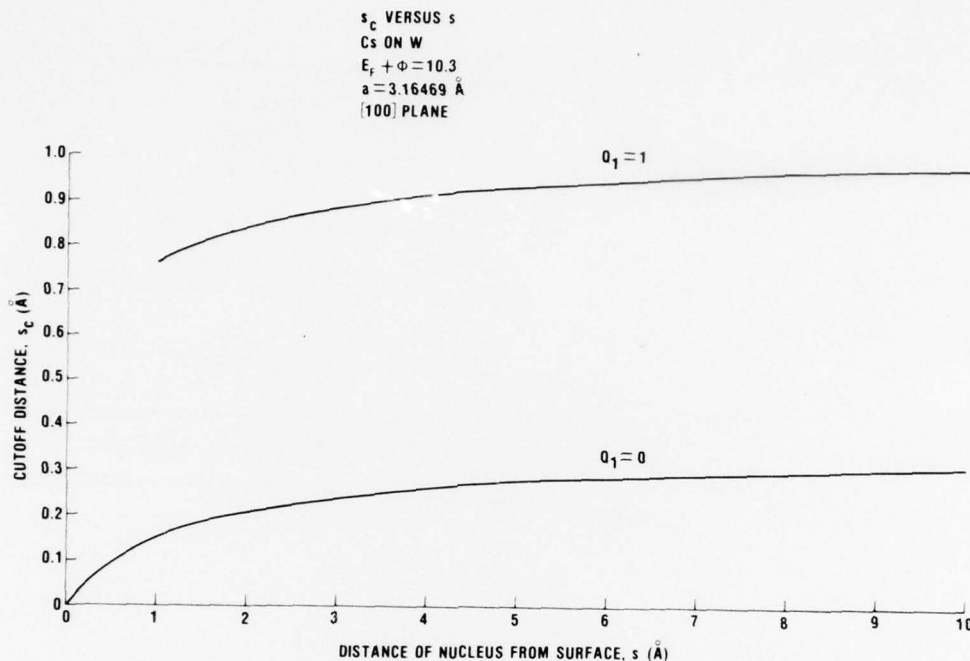


Figure 3. Cutoff parameter for tungsten.

$$\Delta E_i = \frac{\int \psi^* V_i \psi d\tau}{\int \psi^* \psi d\tau}, \quad (6)$$

where

ΔE_i is the energy shift,

* stands for complex conjugation,

τ covers the region $-\infty < x, y < \infty, s_c - s < z < \infty$,

and where

$$V_i = -\frac{q^2}{4(s+z)} + \frac{q^2}{2s+z}. \quad (7)$$

The assumption $R \approx 2s + z$ has been made in equation (7). By using the wave function given by equation (5), the integrals of equation (6) may be evaluated. The result is

$$\begin{aligned}
\Delta E_i = \frac{q^2 \alpha}{4} & \left\{ 4g(2\alpha s) \left(\text{Ei}(4\alpha s) - \text{Ei} \left[2\alpha(s + s_c) \right] \right) \right. \\
& - 4g(-2\alpha s) \text{Ei}(-4\alpha s) - g(\alpha s) \left[\text{Ei}(2\alpha s) - \text{Ei}(2\alpha s_c) \right] \\
& + g(-\alpha s) \text{Ei}(-2\alpha s) + \left[\frac{9}{4} + \frac{3}{2} \alpha(s - s_c) + 25(\alpha s)^2 \right. \\
& \left. \left. - 13\alpha^2 s s_c + 3(\alpha s_c)^2 \right] \exp[-2\alpha(s - s_c)] \right\} / F(s, s_c)
\end{aligned} \tag{8}$$

where

$$g(x) = \left(\frac{1}{2} + x - x^2 + 2x^3 \right) e^{-2x} \tag{9}$$

$$\begin{aligned}
F(s, s_c) = 2 - & \left[1 + \frac{3}{2} \alpha(s - s_c) + \alpha^2(s - s_c)^2 + \alpha^3(s - s_c)^3 \right] \\
& \cdot \exp[-2\alpha(s - s_c)] ,
\end{aligned} \tag{10}$$

$$\text{Ei}(z) = \int_{-\infty}^z \frac{e^{\tau}}{\tau} d\tau . \tag{11}$$

as derived from Abramowitz and Stegun.⁷ The details of the derivation are given in appendix A. This result, equation (8), is to be compared with equation (11) in Gadzuk's paper, which is incorrect. Gadzuk's result should also be multiplied by two if the energy shift is to be given in electron volts, and his figure 4 should have the ordinate doubled.⁴

⁴J. W. Gadzuk, *Surface Science*, 6 (1967), 133.

⁷M. Abramowitz and I. A. Stegun, Ed., *Handbook of Mathematical Functions*, National Bureau of Standards, Gaithersburg, MD (1964).

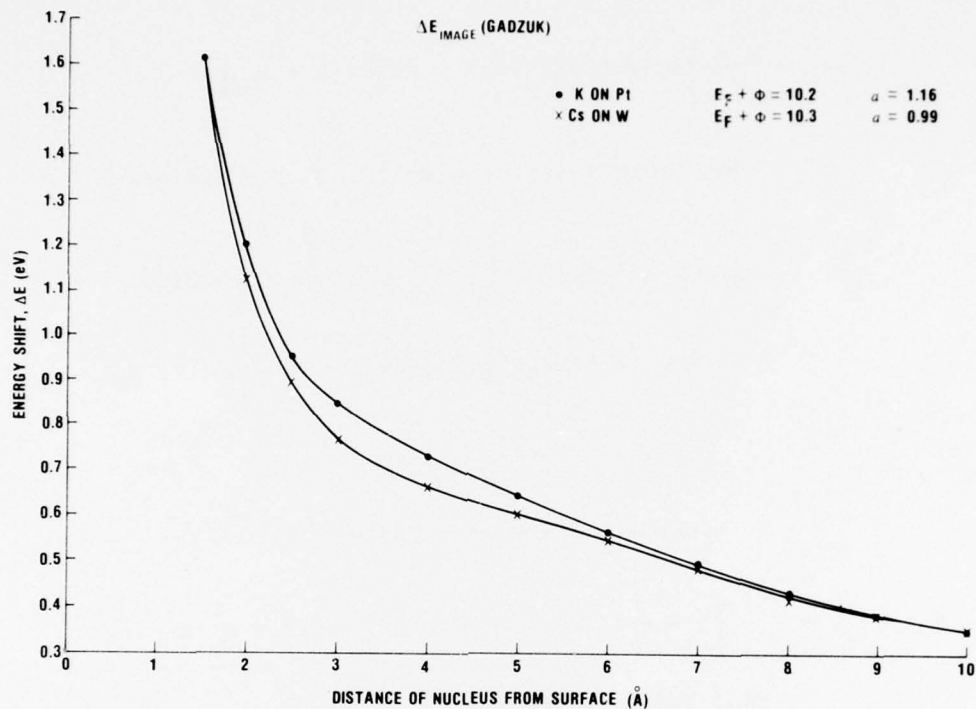


Figure 4. Energy shift in Gadzuk's theory.

The results given in equation (8) are shown in figure 4, which should be compared to Gadzuk's figure 4. These results are quite similar when the factor of two is taken into consideration. Slight changes in the Fermi energy or work function can account for the difference in the results. (Gadzuk did not state the values of the Fermi energy or work function used in his calculations.)

The energy shift given above is that predicted on the basis of classical image theory. We shall now consider the effects of several refinements of the theory.

3. ENERGY SHIFT DUE TO IONIC CHARGES AT SURFACE

3.1 Potential

If we assume that the ion cores of the surface atoms carry a residual charge Q_1 which is neutralized by a continuous background of electrons, then the results in section 2 are significantly altered. In the work reported here, we assume that only these ions on the surface contribute to the potential outside the metal. The charge distribution in the surface (the plane $z = -s$) is assumed to be

$$\sigma(x, y) = \sum_{nm} Q_1 \delta(x - na) \delta(y - ma) - \frac{Q_1}{a^2}, \quad (12)$$

where

σ is the surface charge density,

x, y are coordinates in the surface plane,

a is the lattice constant,

δ is the Dirac delta function, defined by

$$\int \delta(x - x_0) f(x) dx = f(x_0)$$

for body-centered cubic W and

$$\begin{aligned} \sigma(x, y) = \sum_{nm} Q_1 \left\{ \delta(x - na) \delta(y - ma) \right. \\ \left. + \delta\left[x - \left(n + \frac{1}{2}\right)a\right] \delta\left[y - \left(m + \frac{1}{2}\right)a\right] \right\} - \frac{2Q_1}{a^2} \end{aligned} \quad (13)$$

for face-centered cubic Pt. The first terms involving δ -functions represent the ionic point charges, and the last term represents the

continuous electron distribution. The neutrality of the system can be demonstrated by integrating either distribution (eq (12) or (13)) over the area occupied by a single cell. The potential, $V_p(z)$, at the electron on the alkali atom is derived in appendix B. The cutoff condition given by equation (3) is now modified to

$$-V_o = \frac{q^2}{4d_1} + \frac{q^2}{R} + V_p(z), \quad z = s_c - s, \quad (14)$$

which determines s_c . Equation (14) has been used to determine s_c as a function of s for several values of Q_1 (fig. 2, 3). The addition of the potential created by the surface ions tends to lower the barrier near the surface of the metal and thereby decreases the total potential to $-V_o$ at greater distances from the surface.

3.2 Energy Shift

The energy shift given by equation (8) is considerably modified by the inclusion of the ions in the surface of the metal. The surface ions have a large effect on the cutoff near the surface (fig. 2, 3).

A difficulty exists in determining the value of the ionic charge, and, for the purposes here, we have chosen both Pt and W to have a charge of $+e$. Much larger values would be necessary for W if the charge were chosen proportional to the valence of the metal ion.

The calculation of the energy shift due to the point-charge lattice on the surface is straightforward (app C). The result, equation (C-13), must be added to the image contribution, equation (8), to obtain the total energy shift (fig. 5) for K on Pt or Cs on W.

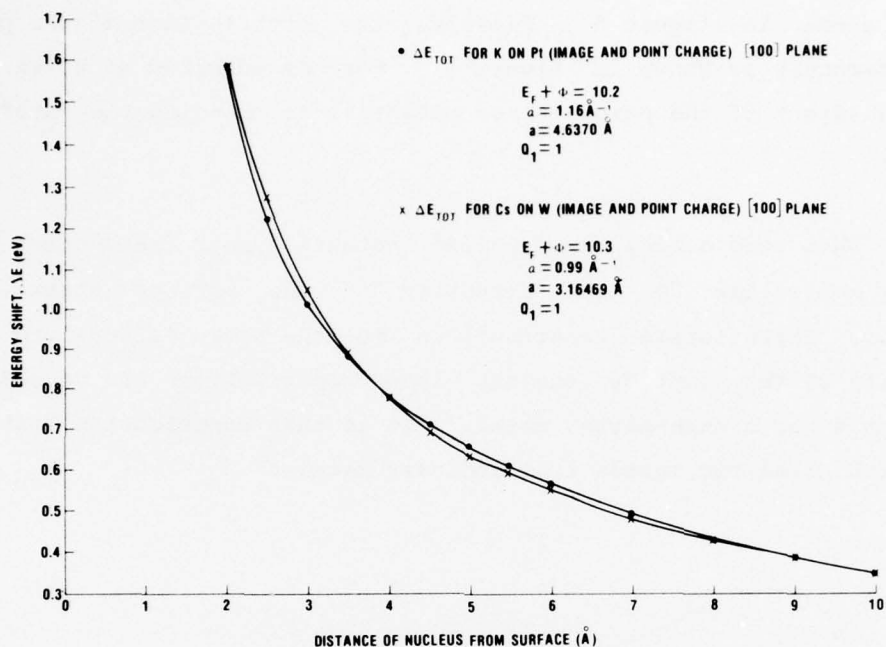


Figure 5. Energy shift including point charge potential.

The energy shift may be decomposed into three parts:

- a. The image shift as calculated by Gadzuk
- b. The change in ΔE_1 due to the change in s_c , as given by equation (14)
- c. The contribution of the point-charge potential

We have plotted these components separately for K adsorbed on Pt. The image shift is given in figure 4. Figure 2 shows the change in s_c for several values of Q_1 . The effect of this change on the energy

shift is shown in figure 6. Finally, the contribution of the point charges directly is shown in figure 7. For Cs adsorbed on W, we have given the effect of the point-charge potential in changing the cutoff in figure 3.

When considering the detailed potential near the surface of a metal, we must allow for the structure of the surface states; in particular, there arise contributions to the potential due to the asphericity of the surface states. These contributions are considered in section 4 for a rare-earth metal. It is this contribution that may distinguish catalytic metals from ordinary metals.

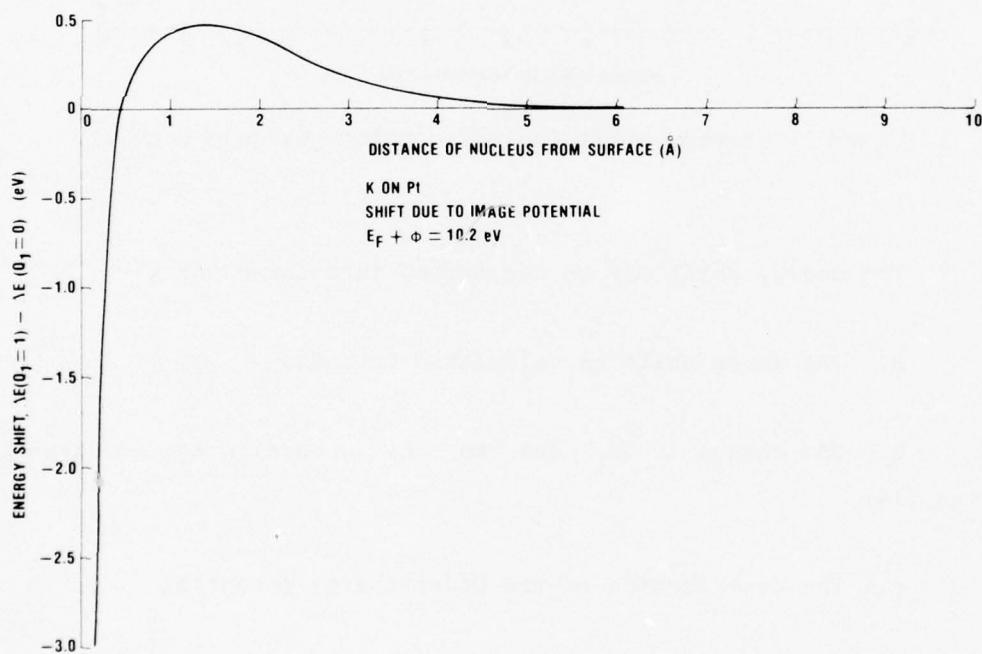


Figure 6. Change in energy shift due to change in cutoff.

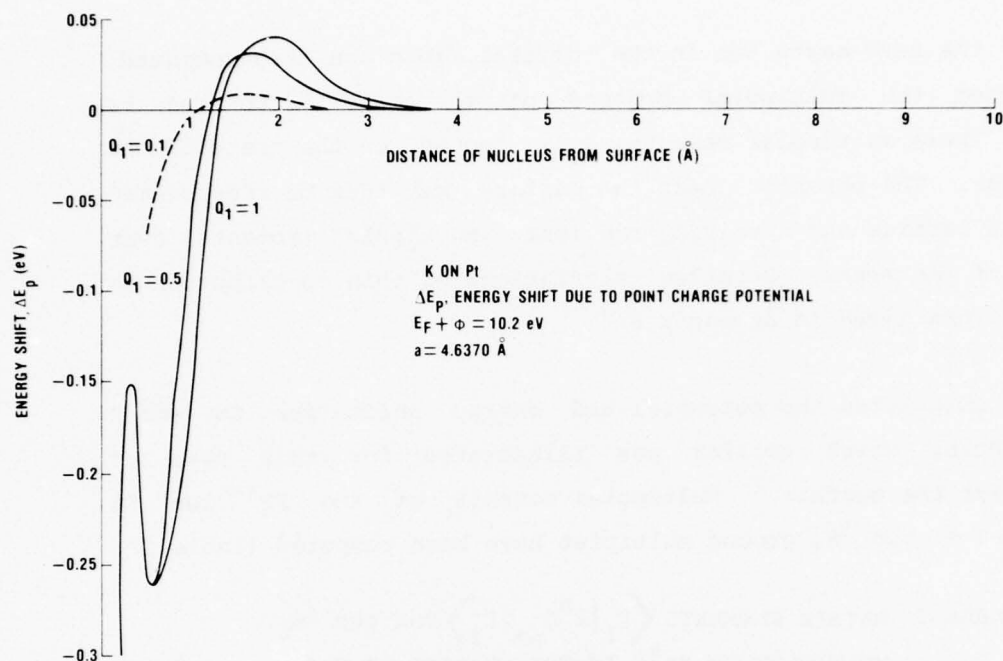


Figure 7. Energy shift due to point charge potential.

4. ENERGY SHIFT DUE TO SURFACE STATES

We now consider those contributions to the potential near the surface of a metal which depend on the detailed surface states of the ions at the surface. For a metal composed of rare-earth ions, this contribution may be done simply, since the f-electrons may be regarded as localized about particular ionic sites. This localization corresponds to the tight-binding approximation in band theory.⁸ We shall take the approach of crystal field theory.⁹ That is, the electric potential near a rare-earth site is given; the energy levels and wave

⁸W. A. Harrison, *Pseudopotentials in the Theory of Metals*, Benjamin, New York (1966).

⁹B. G. Wybourne, *Spectroscopic Properties of Rare Earths*, Intersciences Publishers, New York (1965).

functions of the rare-earth ion in the crystal field are then computed, and from them the multipolar moments of the rare earth can be determined. These multipolar moments, $q_{\ell m}$, depend on the state of the rare-earth ion. The potential near the surface may then be represented in terms of a lattice sum involving the ionic multipolar moments over the surface of the metal. Detailed calculations of this contribution to the potential are given in appendix B.

We have calculated the potential and energy shift for Cs and K adsorbed on PrSb, which earlier was illustrated for this type of potential near the surface.² Multipolar moments of the Pr^{3+} ion in various states of the $^3\text{H}_4$ ground multiplet have been computed (table I).

TABLE I. MATRIX ELEMENTS $\langle \Gamma_i | r^n C_{nm} | \Gamma_i \rangle$ FOR THE $^3\text{H}_4$ MULTIPLY OF Pr^{3+} IN THE SURFACE OF PrSb (\AA UNITS)¹

Energy	Γ	n,m				
		2,0	4,0	4,4	6,0	6,4
0	1	0.06770	-0.02043	-0.00544	-0.03075	0.00730
49.5	3	0.05850	-0.01065	-0.00894	0.00037	-0.00229
150.0	2	0.03277	0.00961	-0.03633	0.03056	-0.03627
252.0	2	0.03050	0.01031	0.03451	0.03046	0.03621
415.0	3	-0.01659	0.02445	0.00661	-0.01895	0.00413
592.0	1	-0.08486	-0.01663	-0.00096	0.00390	0.00064
595.0	1	-0.08417	-0.01673	0.00220	0.00380	-0.00876

¹ For Pr^{3+} , the following values of $\langle r^n \rangle$ have been used:

$$\langle r^2 \rangle = 0.304194 (\text{\AA})^2$$

$$\langle r^4 \rangle = 0.221312 (\text{\AA})^4$$

$$\langle r^6 \rangle = 0.345420 (\text{\AA})^6$$

$$\langle \Gamma_i | r^n C_{nm} | \Gamma_i \rangle = \int d\tau' \Psi_{\Gamma_i}^* (r')^n C_{nm} (r') \Psi_{\Gamma_i} (r').$$

See A. J. Freeman and R. E. Watson, Phys. Rev., 127 (1962), 2058.

²C. A. Morrison, N. Karayianis, and D. E. Wortman, A Possible Use of the Surface States of Transition and Rare-Earth Metal Ions in the Theory of Catalysis, Harry Diamond Laboratories TR-1752 (April 1976).

These have been used with the results of appendix C (eq (C-14)) to obtain energy shifts due to the surface states. These additional shifts are shown in figure 8 for K and figure 9 for Cs.

Figure 10 shows the effect of the surface states in changing the s_c for the ground state of Pr. The condition used to obtain s_c is similar to equation (14), except that the surface-state potential, V_s , is added to the right-hand side. This addition results in a slight change in s_c (fig. 10). Figure 11 shows the total energy shift for K adsorbed on the [100] surface of PrSb. This energy shift includes all the effects considered in sections 2 and 3, as well as the surface-state contributions considered here, with the Pr^{3+} ions in their ground state. Figure 12 gives a similar plot for Cs adsorbed on PrSb.

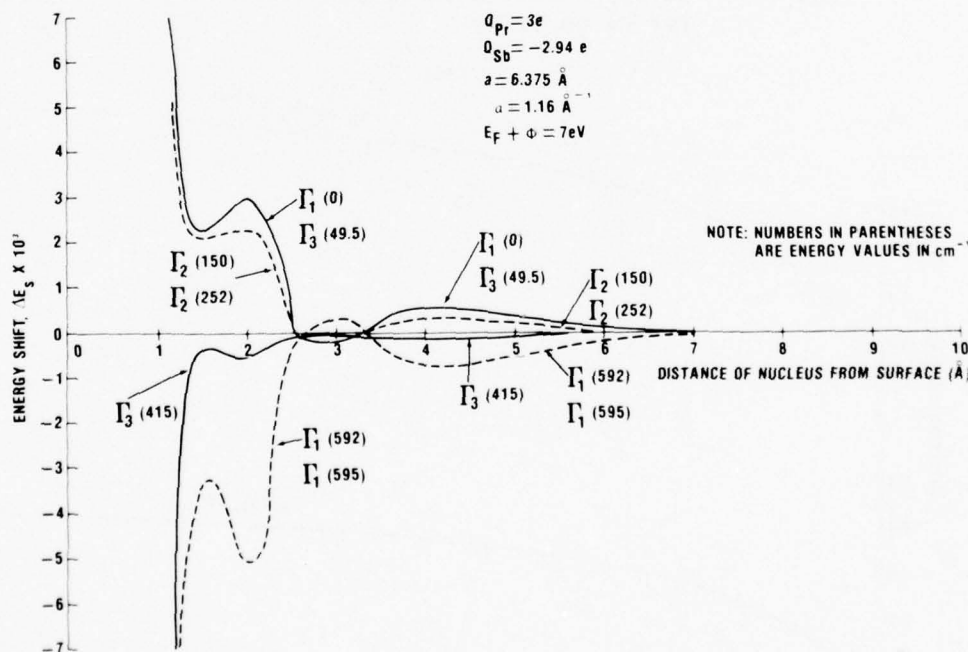


Figure 8. Energy shift in [100] plane due to surface states for K on PrSb.

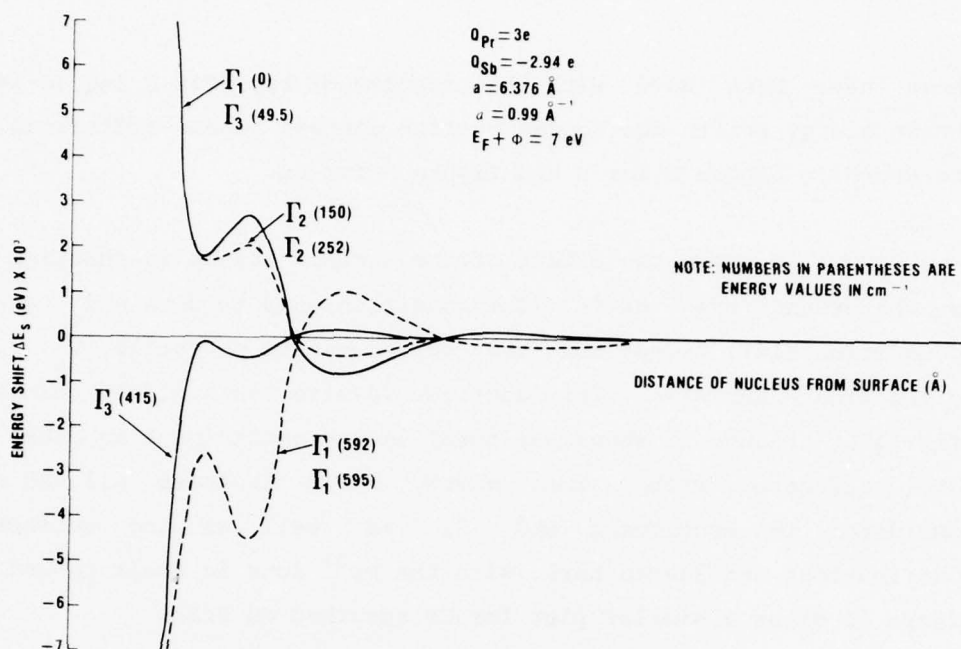


Figure 9. Energy shift in [100] plane due to surface states for Cs on PrSb.

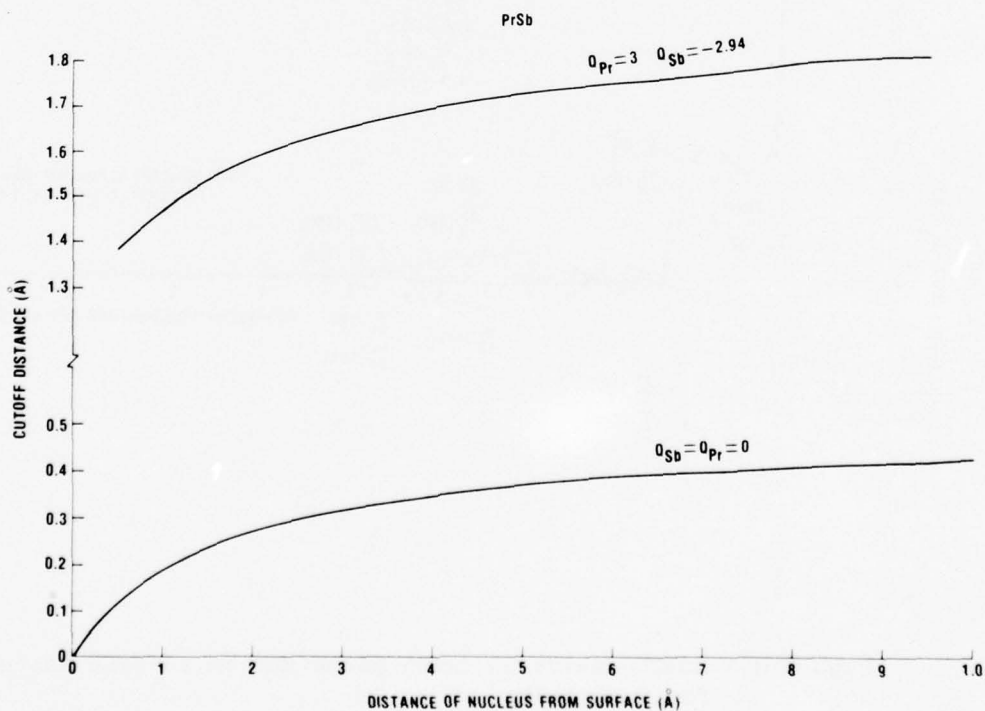


Figure 10. Cutoff parameter for PrSb.

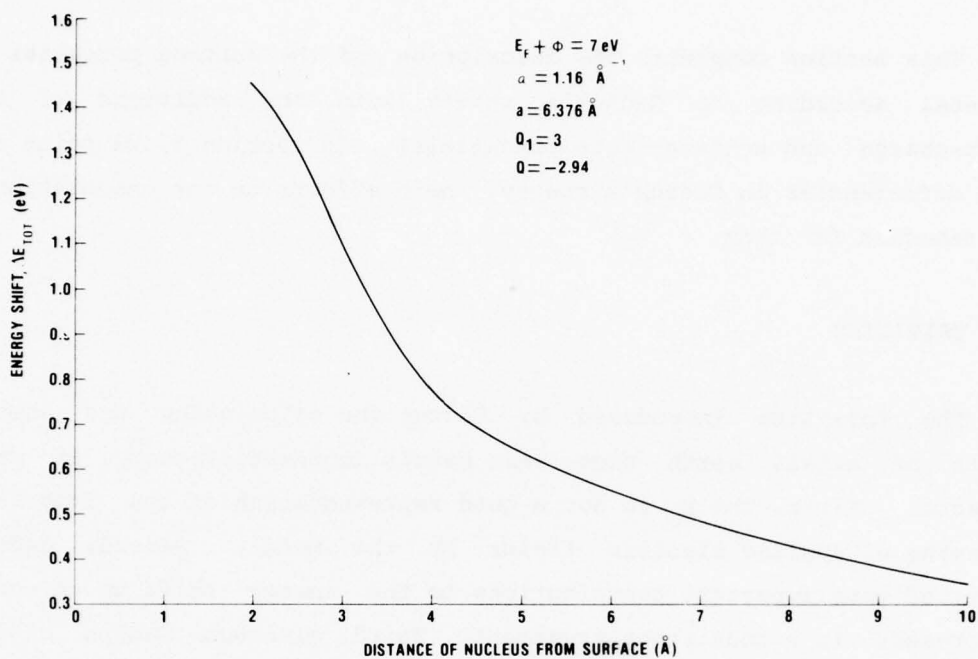


Figure 11. Total energy shift in [100] plane for K on PrSb.

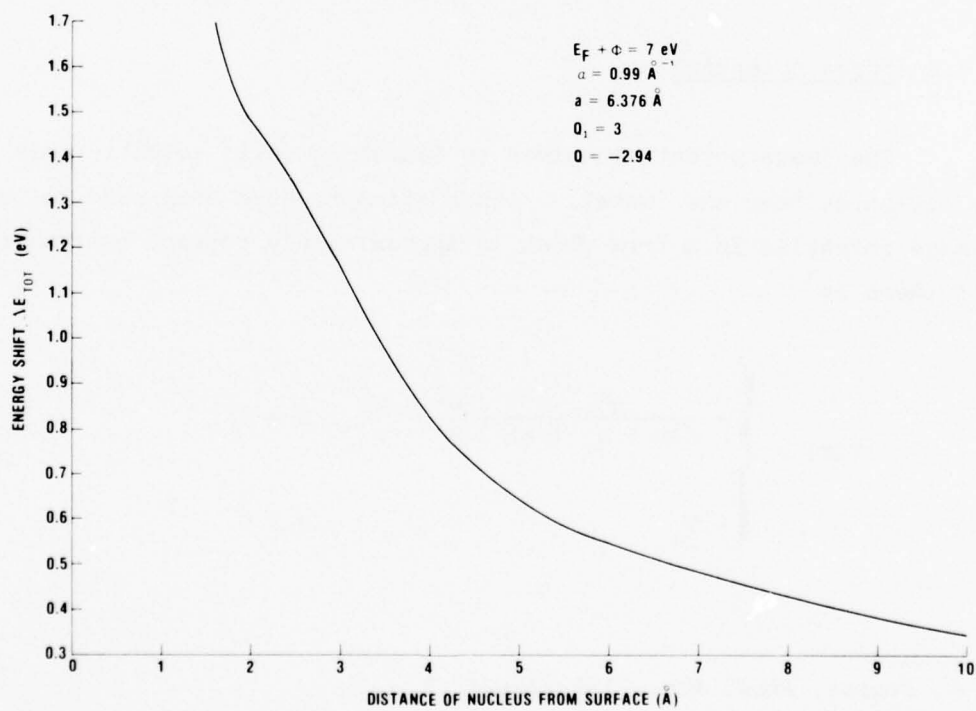


Figure 12. Total energy shift in [100] plane for Cs on PrSb.

This section completes the description of the surface potential of a metal according to Gadzuk's theory (with the additions of the point-charge and surface-state potentials). In section 5, we point out some deficiencies in Gadzuk's theory, their effects on our calculations, and remedies for them.

5. CRITICISM

The formalism introduced by Gadzuk for calculating the energy shifts of alkali earth atoms near metals is unsatisfactory in many respects. First, the s_c is not a good representation of the imperfect screening of applied electric fields by the metal. Second, Gadzuk neglected some important contributions to the energy shift which would be present in a consistent treatment. Third, although Gadzuk claims that his procedure is first-order perturbation theory, the assumption that the wave function vanishes for $z < s_c - s$ is not standard.

5.1 Image Potential

The image potential given by Gadzuk is valid actually only at large distances from the metal. Other attempts have been made to cast the image potential in a form which is approximately correct everywhere. One of these is¹⁰

$$v(r) = \begin{cases} -\frac{q^2}{4(s + s_c + z)} + \frac{q^2}{R} - \frac{q^2}{r}, & z > 0, \\ -V_0, & z < 0, \end{cases} \quad (15)$$

¹⁰F. M. Propst, *Phys. Rev.*, 129 (1962), 7.

in which the s_c is explicit in the potential and is given by

$$s_c = q^2/4V_o . \quad (16)$$

Energy shifts may be calculated by using equation (15) in a manner similar to that used in section 2. However, the conceptual difficulties still remain; the wave function is still truncated (now at $z = -s$ instead of $z = -s + s_c$), and the procedure used to evaluate the shifts is not a standard perturbation technique.

Rather than use these cutoff methods, we may employ a consistent (though still approximate) method of treating the image problem in metals. The simplest such technique is to use the Thomas-Fermi model¹¹ for the dielectric response of the metal. In this theory, the image potential is determined by the partial differential equations

$$\begin{aligned} \nabla^2 \phi(\underline{r}') &= 4\pi q \delta(\underline{r}') - 4\pi q \delta(\underline{r}' - \underline{r}), \quad z' > -s, \\ \nabla^2 \phi(\underline{r}') &= K_{FT}^2 \phi(\underline{r}'), \quad z' < -s, \end{aligned} \quad (17)$$

where

$$K_{FT}^2 = \frac{6\pi N e^2}{E_F} = \left[\frac{12\pi}{(3\pi^2)^{2/3}} \frac{1}{\alpha_o} \right] N^{1/3} .$$

with N the number of free electrons per unit volume and α_o the Bohr radius. The total electrostatic energy is then obtained from equation (17) by calculating the total work necessary to bring the charges to their respective positions from infinity.

¹¹D. Pines, *Elementary Excitations in Solids*, Benjamin, New York (1963), 96.

5.2 Renormalization Terms

In the analysis presented by Gadzuk, first-order perturbation theory was applied only to the interaction potential with the wave functions normalized in the region $z > s_c - s$. An additional shift arises if one considers the unperturbed Hamiltonian

$$H_0 = T - \frac{g^2}{r} , \quad (18)$$

where

$$T = \frac{p^2}{2m}$$

and p is the momentum operator, and if one evaluates the matrix of H_0 using the perturbed wave functions. If then the matrix elements of H_0 for large s are subtracted out, an additional shift is obtained, or

$$\Delta E_n = \frac{\langle s | H_0 | s \rangle}{\langle s | s \rangle} - \langle \infty | H_0 | \infty \rangle , \quad (19)$$

where

$$\langle s | H_0 | s \rangle = \int_{s_c - s}^{\infty} dz \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^* H_0 \psi dx dy \quad (20)$$

and

$$\langle s | s \rangle = \int_{s_c - s}^{\infty} dz \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^* \psi dx dy . \quad (21)$$

By using the wave function given in equation (6), the result is

$$\Delta E_n = (3.81\alpha^2 + 3.60\alpha) f[\alpha(s - s_c)] , \quad (22)$$

where

$$f(x) = \frac{e^{-2x} \left(\frac{3}{2} x - x^2 + x^3 \right)}{1 - e^{-2x} \left(\frac{1}{2} + \frac{3}{4} x + \frac{x^2}{2} + \frac{x^3}{2} \right)} \quad (23)$$

Equation (23) was used to calculate ΔE_n for the two cases considered by Gadzuk (fig. 13). A comparison of these results with those of figure 4 shows that at $s = 3 \text{ \AA}$ the ΔE_n is approximately 63 percent of the result given in figure 4. The corresponding quantity at $s = 4 \text{ \AA}$ is still approximately 20 percent. (Gadzuk chose the region $s = 3, 4 \text{ \AA}$, for comparison of his results to reported data.) In this region, the contribution of ΔE_n is certainly not negligible.

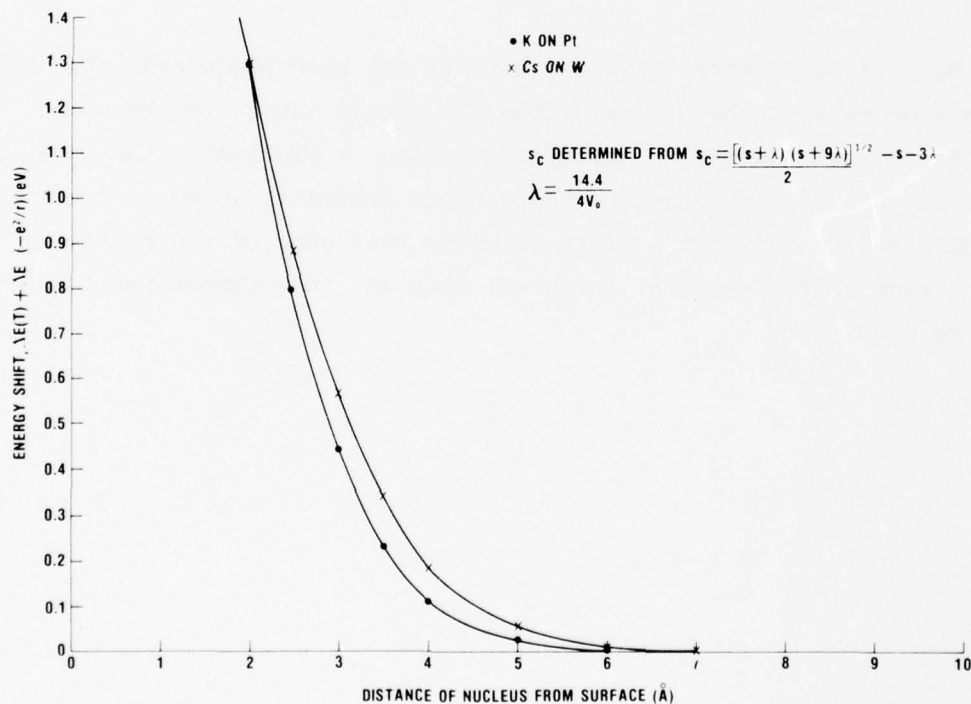


Figure 13. Energy shift due to wave-function renormalization.

6. DISCUSSION AND CONCLUSION

The energy shift of alkali earth atoms near metals has been calculated based on a modified version of Gadzuk's theory. This energy shift includes image effects and effects due to the ionic pseudopotential and the state of the ions at the surface. We have found several errors in Gadzuk's paper which, when corrected, alter some of the consequences of that work. We have found shifts in energy of about 0.6 eV at distances of several angstroms from the metal surfaces, which is a factor of two higher than shifts found by Gadzuk. Finally, we have shown that Gadzuk's theory is incomplete in that it neglects wave-function renormalization effects, and we have proposed an alternative model, the Thomas-Fermi model, for image forces in the metal.

What is of primary interest, but has not been addressed yet, is the transition rate of the electron from the alkali atom to the metal. To calculate this quantity to a sufficient rate or precision, the potential seen by the electron must be known quite accurately. We conclude that Gadzuk's theory does not permit accurate knowledge of the potential and that a more self-consistent treatment such as the Thomas-Fermi method must be used.

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SYMBOLS

a	lattice constant
α_o	Bohr radius
B_{nm}	crystal field parameter
E_F	Fermi energy
\hbar	Planck's constant
H	single electron Hamiltonian
m	electron mass
N	number of free electrons per unit volume
p	momentum operator
q	electron charge
Q_l	residual charge
r	ion core
R	ion image
s	distance of nucleus from surface
s_c	cutoff distance
V_i	interaction energy
V_o	sum of Fermi energy and work function
$V_p(z)$	electrostatic potential energy
V_s	surface-state potential
x, y, z	coordinates normal to metal surface
δ	Dirac delta function
ΔE_i	energy shift

SYMBOLS (CONT'D)

ΔE_n	energy shift due to renormalization
σ	surface-charge density
ϕ	work function
*	complex conjugation
∇^2	Laplacian operator

APPENDIX A.--ENERGY SHIFT IN GADZUK'S THEORY

In this appendix, we derive the energy shift due to the image charges as originally presented by Gadzuk.¹ We set up a coordinate system centered about the ion core of the ad-atom, with the z-axis normal to the surface of the metal. In this coordinate system, the nucleus is at (0,0,0) (fig. 1 in main body of report), and the electron is at point $\underline{r} = (x,y,z)$. The image potential (ϕ_{image}) at point \underline{r} due to charge q at \underline{r}' with an ideal metal to the left of plane $z = -s$ is given by

$$\phi_{\text{image}} = \frac{q}{|\underline{r} - \underline{r}'|} - \frac{q}{|\underline{r} + 2\underline{s} - \underline{r}''|}, \quad (\text{A-1})$$

where

$$\begin{aligned} \underline{s} &= \hat{e}_z s, \\ \underline{r}'' &= (x', y', -z'). \end{aligned}$$

If we have an assembly of charges, the total potential energy of the system is equal to the total work done in bringing the charges to their positions from infinity. From equation (A-1), we calculate, for the system of figure A-1,

$$U_i = -\frac{q^2}{r} - \frac{q^2}{4(s+z)} + \frac{q^2}{|2\underline{s} + \underline{r}|} - \frac{q^2}{4s}, \quad (\text{A-2})$$

¹J. W. Gadzuk, *Surface Science*, 6 (1967), 159.

APPENDIX A

where

U_i is the total potential energy,

q is the electronic charge,

r is the ion core,

s is the distance of the nucleus from the surface.

In equation (A-2), the first term represents the direct electron-ion interaction; the second is the interaction of the electron with its own image; the third is the interaction of the electron with the ion image; and the last is the ion-ion image interaction. The first term is included in the unperturbed Hamiltonian, while the last term does not depend on the electron coordinates.

Finally, we make the approximation $|2s + \underline{r}| \approx (2s + z)$ in the third term in equation (A-2). Therefore, the second and third terms in equation (A-2) are

$$V_i = - \frac{q^2}{4(s + z)} + \frac{q^2}{2s + z}, \quad (\text{A-3})$$

(where V_i is the interaction energy) which is the form used by Gadzuk.

In calculating the energy shift due to the potential of equation (A-3), Gadzuk made the additional assumption that the electron wave function vanishes for $z < s_c - s$, where s_c , the cutoff parameter, is given by

$$V_i(z) \Big|_{z=s_c-s} = -V_o, \quad (\text{A-4})$$

where V_o is the sum of the Fermi energy, E_F , and the work function, ϕ . Equation (A-4) yields the following result for s_c :

$$s_c = \frac{1}{2} \left\{ [(s + \lambda)(s + 9\lambda)]^{1/2} - s - 3\lambda \right\}, \quad (\text{A-5})$$

where

$$\lambda = q^2/4V_0 = 3.6/V_0 ,$$

V_0 is in electron volts,

λ is in angstrom units.

The electron wave function is taken as

$$\psi(r) = N(1 - \alpha r)e^{-\alpha r} , \quad (A-6)$$

where

ψ is the wave function,

N is the normalization constant,

and ψ is assumed to vanish for $z < s_c - s$. Therefore, N is given by

$$\frac{1}{N^2} = 2\pi \int_{s_c-s}^{\infty} dz \int_0^{\infty} \rho d\rho (1 - \alpha r)^2 e^{-2\alpha r} , \quad (A-7)$$

where $r = (\rho^2 + z^2)^{1/2}$. The energy shift is obtained by first-order perturbation theory:

$$\Delta E_i = 2\pi N^2 \int_{s_c-s}^{\infty} dz V_i(z) \int_0^{\infty} \rho d\rho (1 - \alpha r)^2 e^{-2\alpha r} , \quad (A-8)$$

where ΔE_i is the energy shift. The integral over ρ may be easily performed by making the substitution $\rho = r - z$. The result is

$$\Delta E_i = e^2 \frac{\int_{s_c-s}^{\infty} dz F(|z|) \left[\frac{1}{2s+z} - \frac{1}{4(s+z)} \right]}{\int_{s_c-s}^{\infty} dz F(|z|)} , \quad (A-9)$$

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where

$$F(z) = \frac{1}{4\alpha^2} e^{-2\alpha z} \left(\frac{1}{2} + \alpha z - \alpha^2 z^2 + 2\alpha^3 z^3 \right), \quad (A-10)$$

and the z -integrals may be performed to give

$$\begin{aligned} \Delta E_i = \frac{e^2 \alpha}{4} & \left\{ 4g(2\alpha s) [Ei(4\alpha s) - Ei[2\alpha(s + s_c)]] \right. \\ & - 4g(-2\alpha s) Ei(-4\alpha s) - g(\alpha s) [Ei(2\alpha s) - Ei(2\alpha s_c)] \\ & + g(-\alpha s) Ei(-2\alpha s) + \left[\frac{9}{4} + \frac{3\alpha}{2} (s - s_c) + 25(\alpha s)^2 \right. \\ & \left. \left. - 13\alpha^2 s s_c + 3(\alpha s_c)^2 \right] \exp[-2\alpha(s - s_c)] \right\} / \\ & \left\{ 2 - \exp[-2\alpha(s - s_c)] \left[1 + \frac{3\alpha}{2} (s - s_c) + \alpha^2 (s - s_c)^2 + \alpha^3 (s - s_c)^3 \right] \right\}, \end{aligned} \quad (A-11)$$

where $g(x) = \left(\frac{1}{2} + x - x^2 + 2x^3 \right) e^{-2x}$. This is the form used in the main body of this report. In equation (A-11), the exponential integral is

$$Ei(x) = \int_{-\infty}^x \frac{dte^t}{t}.$$

Several convenient forms for computation are given by Abramowitz and Stegun.²

²M. Abramowitz and I. A. Stegun, ed., *Handbook of Mathematical Functions*, National Bureau of Standards, Gaithersburg, MD (1964).

SYMBOLS

\hat{e}_z	unit vector in z direction
E_F	Fermi energy
q	electronic charge
r	ion core
\tilde{r}	distance to point
s, \tilde{s}	distance of nucleus from surface
s_c	cutoff parameters
U_i	total potential energy
V_i	interaction energy
V_o	sum of Fermi energy and work function
ΔE_i	energy shift
ϕ_{image}	image potential
ϕ	work function
ψ	wave function

APPENDIX B.--POTENTIAL DUE TO IONS IN SOLID

B-1. INTRODUCTION

In this appendix, we discuss two contributions to the electrostatic potential outside a metal surface. One contribution is due to the lattice of point charges and the uniform background of the electron gas. The second contribution is due to the asphericity of the ions constituting the solid; this asphericity depends on the electronic state of the ions.

B-2. POINT-CHARGE LATTICE SUM

In discussing the first contribution to the potential, we consider a rectangular lattice with lattice constants a and b . It is assumed that a point charge, Qq , is situated at the center of each unit cell. At the same time, we consider a uniform background of magnitude $\sigma = -Qq/ab$. It is necessary to consider both these contributions together in order to obtain finite results.

We consider only the first layer of point charges in the metal. We may do so since screening by the electron gas is expected to reduce the contributions of other layers considerably, and even without this screening the contributions due to the other layers are small, as shown by detailed calculations. We assume that the first layer is not screened at all.

To properly handle the divergence problems inherent in the calculation of the potential, we consider a finite system consisting of $(2R_1 + 1)$ unit cells in the x -direction and $(2R_2 + 1)$ unit cells in the y -direction. The origin of coordinates is taken at the center of the

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lattice; we assume one ion at the center of each unit cell. The total electrostatic potential energy (V_p) of a charge $-q$ at the point (x, y, z) is then given by

$$V_p(x, y, z) = \sum_{p=-R_1}^{+R_1} \sum_{q'=-R_2}^{+R_2} \frac{-Qq^2}{[(x - pa)^2 + (y - q'b)^2 + z^2]^{\frac{1}{2}}} + \int_{-a(R_1+\frac{1}{2})}^{a(R_1+\frac{1}{2})} dx' \int_{-b(R_2+\frac{1}{2})}^{b(R_2+\frac{1}{2})} dy' \cdot \frac{Qq^2}{ab[(x - x')^2 + (y - y')^2 + z^2]^{\frac{1}{2}}} \quad (B-1)$$

The first term in equation (B-1) is due to the point-charge lattice, and the second is due to the uniform background. We are interested in evaluating equation (B-1) in the limit $R_1, R_2 \rightarrow \infty$.

Equation (B-1) may be transformed to a more convenient form by making the substitution

$$\frac{1}{[(x - pa)^2 + (y - q'b)^2 + z^2]^{\frac{1}{2}}} = \frac{1}{\sqrt{\pi}} \int_0^\infty t^{-\frac{1}{2}} dt \exp \left\{ -t [(x - pa)^2 + (y - q'b)^2 + z^2] \right\} \quad (B-2)$$

Now we must consider sums of the form

$$S(t) = \sum_{p=-R_1}^{+R_1} \exp[-t(x - pa)^2] \quad (B-3)$$

and use the method of converting such sums given by Whittaker and Watson.¹ Consider the function $f(z) = \exp[-t(x - za)^2]$ in the complex plane. By considering the contour shown in figure B-1, we may show that

$$S(t) = \oint_C \frac{dz f(z)}{e^{2\pi iz} - 1} =$$

$$\lim_{\epsilon \rightarrow 0} \int_{-R_1 - \frac{1}{2}}^{R_1 + \frac{1}{2}} \frac{dx' f(x')}{e^{2\pi i(x' - i\epsilon)} - 1} - \int_{-R_1 - \frac{1}{2}}^{R_1 + \frac{1}{2}} \frac{dx' f(x')}{e^{2\pi i(x' + i\epsilon)} - 1}. \quad (B-4)$$

Now we may expand the denominators in equation (B-4) and take the limit. We obtain

$$S(t) = \sum_{p=-\infty}^{\infty} \int_{-R_1 - \frac{1}{2}}^{R_1 + \frac{1}{2}} dx' f(x') e^{-2\pi i p x'}. \quad (B-5)$$

Now we consider the sum in equation (B-1). We substitute equation (B-2) into equation (B-1) and use equation (B-5) to obtain

$$V_P(x, y, z) = - \sum_{p, q'=-\infty}^{\infty} Qq'^2 \int_0^{\infty} \frac{t^{-\frac{1}{2}} dt}{\sqrt{\pi}} \exp(-tz^2)$$

$$\cdot \int_{-R_1 - \frac{1}{2}}^{R_1 + \frac{1}{2}} dx' e^{-2\pi i p x'} \int_{-R_2 - \frac{1}{2}}^{R_2 + \frac{1}{2}} dy' e^{-2\pi i q' y'}$$

$$\cdot \exp\left\{-t[(x - x'a)^2 + (y - y'b)^2]\right\}$$

$$+ Qq'^2 \int_{-a(R_1 + \frac{1}{2})}^{a(R_1 + \frac{1}{2})} dx' \int_{-b(R_2 + \frac{1}{2})}^{b(R_2 + \frac{1}{2})} dy' \frac{1}{ab[(x - x')^2 + (y - y')^2 + z^2]^{\frac{1}{2}}}. \quad (B-6)$$

¹E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis*, University Press, Cambridge, U.K. (1950), 124.

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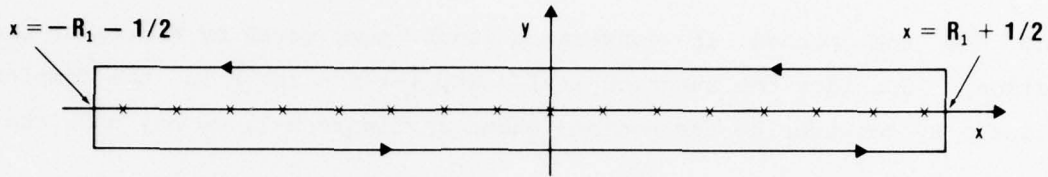


Figure B-1. Contour used for integral.

Now we consider this expression in the limit as R_1 and R_2 become infinite. The integrals over t converge in the limit except for the integral with $p = q' = 0$. We consider this term separately. We have

$$\begin{aligned}
 & -Qq^2 \int_0^\infty \frac{t^{-1/2} dt}{\sqrt{\pi}} \exp(-tz^2) \int_{-R_1-1/2}^{R_1+1/2} dx' \int_{-R_2-1/2}^{R_2+1/2} dy' \\
 & \cdot \exp\left\{-t[(x - x'a)^2 + (y - y'b)^2]\right\} = \quad (B-7) \\
 & -Qq^2 \int_{-R_1-1/2}^{R_1+1/2} dx' \int_{-R_2-1/2}^{R_2+1/2} dy' \frac{1}{[(x - x'a)^2 + (y - y'b)^2]^{1/2}},
 \end{aligned}$$

and this contribution cancels the last integral in equation (B-6). In the remainder of equation (B-6), we may immediately take the limit $R_1, R_2 \rightarrow \infty$. We have

$$\int_{-\infty}^\infty dx' e^{-2\pi i p x'} \exp[-t(x - x'a)^2] = \frac{1}{a} \sqrt{\frac{\pi}{t}} \exp\left[-\frac{\pi^2 p^2}{ta^2} - \frac{2\pi i p x}{a}\right], \quad (B-8)$$

with a similar result for the y' integration. Therefore, we obtain

$$\begin{aligned}
 v_p(x, y, z) = & -\frac{Qq^2}{ab} \sum_{p, q'=-\infty}^\infty \exp\left[-2\pi i \left(\frac{px}{a} + \frac{q'y}{b}\right)\right] \\
 & \cdot \sqrt{\pi} \int_0^\infty t^{-3/2} dt \exp\left[-tz^2 - \frac{\pi^2}{t} \left(\frac{p^2}{a^2} + \frac{q'^2}{b^2}\right)\right] \quad (B-9)
 \end{aligned}$$

where the prime sign on the summation in equation (B-9) indicates that the term $p=q'=0$ is to be omitted. The integral in equation (B-9) may be performed to obtain

$$V_p(x, y, z) = -\frac{Qq^2}{ab} \sum_{p, q'=-\infty}^{\infty} \left(\frac{p^2}{a^2} + \frac{q'^2}{b^2} \right)^{-\frac{1}{2}} \cdot \exp \left[-2\pi i \left(\frac{px}{a} + \frac{q'y}{b} \right) - 2\pi |z| \left(\frac{p^2}{a^2} + \frac{q'^2}{b^2} \right)^{\frac{1}{2}} \right]. \quad (B-10)$$

This is the final result.

B-3. CONTRIBUTION OF SURFACE STATES

We now consider those contributions to the surface potential which depend on the states of the ions at the surface of the metal. Consider an ion whose center is on the lattice at the point

$$\mathbf{R}_i = \hat{e}_x pa + \hat{e}_y q'b, \quad (B-11)$$

where \mathbf{R}_i is the vector from the origin to the ion, \hat{e}_x and \hat{e}_y are unit vectors in the x and y directions, respectively, and an electron associated with the ion at distance \mathbf{r}' relative to \mathbf{R}_i . Then the potential ϕ_i , at point \mathbf{r} due to this electron is given by

$$\phi_i = -\frac{q}{|\mathbf{R}_i + \mathbf{r}' - \mathbf{r}|} = -\sum_{\ell, m} \frac{q(r')^\ell (-1)^\ell}{|\mathbf{R}_i - \mathbf{r}|^{\ell+1}} C_{\ell m}^\dagger(\hat{\mathbf{r}}') C_{\ell m}(\widehat{\mathbf{R}_i - \mathbf{r}}), \quad (B-12)$$

where $\hat{\mathbf{r}}'$ and $\widehat{\mathbf{R}_i - \mathbf{r}}$ are unit vectors in the direction of \mathbf{r}' and $\mathbf{R}_i - \mathbf{r}$, respectively, and the $C_{\ell m}$ are related to the spherical harmonics by

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$C_{\ell m} = [4\pi/(2\ell + 1)]^{1/2} Y_{\ell m}$ as defined elsewhere.² Now we assume that the ion is in a certain state and that the potential due to the ion may be obtained by summing equation (B-12) over all the electrons in the ion and taking the expectation value of the result over the ion state. We therefore obtain, for the potential at r ,

$$\phi_i(r) = q \sum_{\ell, m} \frac{(-1)^\ell q_{\ell m}^+ C_{\ell m}(\hat{R}_i - \underline{r})}{|\hat{R}_i - \underline{r}|^{\ell+1}}, \quad (B-13)$$

where

$$q_{\ell m} = - \sum_e \langle \psi | r^\ell C_{\ell m}(\hat{r}') | \psi \rangle.$$

Quantity $q_{\ell m}$ is thus a function of the state of the surface ion. The $\ell = 0$ part of equation (B-13) is the point-charge lattice sum considered in section B-2.

For the other terms in equation (B-13), we assume that all the surface ions are in the same state. We therefore obtain, for the potential energy, V_s , of an electron at \underline{r} ,

$$V_s(\underline{r}) = -q^2 \sum_{\ell, m, i} \frac{(-1)^\ell q_{\ell m}^+ C_{\ell m}(\hat{R}_i - \underline{r})}{|\hat{R}_i - \underline{r}|^{\ell+1}}. \quad (B-14)$$

The sum over i in equation (B-14) is a lattice sum similar to that considered earlier. It may be converted to a more convenient form by the same techniques illustrated in section B-2 for the point-charge sum. The result is

²C. A. Morrison, N. Karayianis, and D. E. Wortman, *A Possible Use of the Surface States of Transition and Rare-Earth Metal Ions in the Theory of Catalysis*, Harry Diamond Laboratories TR-1752 (April 1976).

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$$\begin{aligned}
 v_s(r) = & -\frac{q^2}{ab} \sum_{\ell, m, p, q'} (2\pi)^\ell q_{\ell m} \left(\frac{p^2}{a^2} + \frac{q'^2}{b^2} \right)^{\frac{\ell - |m| - 1}{2}} \\
 & \cdot \exp \left[-2\pi i \left(\frac{px}{a} + \frac{q'y}{b} \right) - 2\pi |z| \left(\frac{p^2}{a^2} + \frac{q'^2}{b^2} \right)^{\frac{1}{2}} \right] \\
 & \cdot [(\ell - m)! (\ell + m)!]^{\frac{1}{2}} \begin{cases} (-1)^m \left(\frac{q'}{b} - i \frac{p}{a} \right)^m, & m \geq 0 \\ \left(\frac{q'}{b} + i \frac{p}{a} \right)^{|m|}, & m < 0 \end{cases} \quad (B-15)
 \end{aligned}$$

SYMBOLS

a, b	lattice constants
\hat{e}_x, \hat{e}_y	unit vectors in x and y directions
p	momentum operator
Qq	point charge
\underline{r}	point
\hat{r}'	unit vector in direction of \underline{r}'
$\widehat{\underline{R}_i - \underline{r}}$	unit vector in direction of $\underline{R}_i - \underline{r}$
\underline{R}_i	vector from origin to ion
V_p	electrostatic potential energy
V_s	potential energy
x, y, z	} coordinates normal to metal surface
x', y', z'	
σ	magnitude
ϕ_i	potential
Φ	work function
ψ	wave function

APPENDIX C. ENERGY SHIFT DUE TO POINT-CHARGE AND SURFACE-STATE POTENTIALS

In calculating the energy shift due to the ions in the metal, for each type of ion on the surface, we must consider sums of the type shown in equations (B-10) and (B-15) in appendix B of this report. The coordinates of the ion in the unit cell relative to some arbitrary origin are contained in the x and y in these equations. There are three contributions to the x and y :

a. Coordinates of the nucleus of the ad-atom relative to the origin of the lattice, x_o, y_o

b. Coordinates of the lattice ions in the unit cell relative to the origin, x_i, y_i

c. Coordinates of the ad-atom electron relative to the nucleus, x, y

Thus, the term $[(px/a) + (q'y/b)]$ in equations (B-10) and (B-15) is to be replaced by

$$\left[\frac{p}{a} (x + x_o - x_i) + \frac{q'}{b} (y + y_o - y_i) \right].$$

For the PrSb lattice in the [100] plane, the ad-atom is directly above a Pr ion. In this example, the lattice is square ($a = b$); for the [100] plane, Pr ions are at

$$x_1 = 0, y_1 = 0,$$

(C-1)

$$x_2 = a/2, y_2 = a/2.$$

APPENDIX C

The Sb ions are at

$$\begin{aligned}x_3 &= 0, y_3 = a/2, \\x_4 &= a/2, y_4 = 0.\end{aligned}\tag{C-2}$$

Since the ad-atom is directly over a Pr ion, $x_0 = y_0 = 0$. There is a sum over i (1, 2, 3, 4) in equations (B-10) and (B-15); the $q_{\ell m}$ are functions of i . For PrSb, we take $q_{\ell m}(1) = q_{\ell m}(2)$ and $q_{\ell m}(3) = q_{\ell m}(4) = 0$. For Pt and W, we ignore the surface-state contribution and consider simply the point-charge potential. We have Pt ions at the [100] plane:

$$\begin{aligned}x_1 &= 0, y_1 = 0, \\x_2 &= a/2, y_2 = a/2,\end{aligned}\tag{C-3}$$

and for W we have one ion per unit cell for the [100] plane, at $x_1 = y_1 = 0$.

For these simple lattices, the sum over i can be simplified. For Pt, we take only terms with $(p + q')$ even and $(p + q')$ odd in equations (B-10) and (B-15) and multiply the result by 2. For PrSb, we take the sum of the $(p + q')$ even and $(p + q')$ odd terms for the Pr ions and the difference of the $(p + q')$ even and $(p + q')$ odd terms for the Sb ions and multiply both Pr and Sb by 2. Doing so removes the i sum and eliminates the dependence of equations (B-10) and (B-15) on the unit-cell coordinates.

To obtain the energy shift due to these terms, we consider the expectation value of the function

$$g(r) = \exp \left[-2\pi i \left(\frac{px}{a} + \frac{q'y}{b} \right) - 2\pi z \left(\frac{p^2}{a^2} + \frac{q'^2}{b^2} \right)^{1/2} \right], \tag{C-4}$$

when z is now measured relative to the nucleus of the ad-atom. We need the integral

$$\int_0^{2\pi} d\phi \int_{s_c}^{\infty} dz \int_0^{\infty} \rho d\rho (1 - \alpha r)^2 e^{-2\alpha r} g(\underline{r}) \equiv \frac{\pi}{2\alpha^3} G(s - s_c, \alpha, p, q'). \quad (C-5)$$

The angular integral is

$$\int_0^{2\pi} d\phi \exp \left[-2\pi \left(\frac{px}{a} + \frac{q'y}{b} \right) \right] = 2\pi J_0 \left[2\pi \rho \left(\frac{p^2}{a^2} + \frac{q'^2}{b^2} \right)^{1/2} \right], \quad (C-6)$$

where J_0 is the Bessel function of zero order and the ρ integrals may be performed by substituting $\rho = (r^2 - z^2)^{1/2}$ into equation (C-5). We use the relations

$$\int_1^{\infty} x dx e^{-\alpha x} J_0 [\beta (x^2 - 1)^{1/2}] = \left[\frac{\alpha}{\alpha^2 + \beta^2} + \frac{\alpha}{(\alpha^2 + \beta^2)^{3/2}} \right] e^{-(\alpha^2 + \beta^2)^{1/2}}, \quad (C-7)$$

$$\begin{aligned} \int_1^{\infty} x^2 dx e^{-\alpha x} J_0 [\beta (x^2 - 1)^{1/2}] &= \left[\frac{3\alpha^2}{(\alpha^2 + \beta^2)^{5/2}} + \frac{3\alpha^2}{(\alpha^2 + \beta^2)^2} \right. \\ &\quad \left. + \frac{\alpha^2 - 1}{(\alpha^2 + \beta^2)^{3/2}} - \frac{1}{\alpha^2 + \beta^2} \right] e^{-(\alpha^2 + \beta^2)^{1/2}} \end{aligned} \quad (C-8)$$

$$\begin{aligned} \int_1^{\infty} x^3 dx e^{-\alpha x} J_0 [\beta (x^2 - 1)^{1/2}] &= \left[\frac{15\alpha^3}{(\alpha^2 + \beta^2)^{7/2}} + \frac{15\alpha^3}{(\alpha^2 + \beta^2)^3} + \frac{6\alpha^3 - 9\alpha}{(\alpha^2 + \beta^2)^{5/2}} \right. \\ &\quad \left. + \frac{\alpha^3 - 9\alpha}{(\alpha^2 + \beta^2)^2} - \frac{3\alpha}{(\alpha^2 + \beta^2)^{3/2}} \right] e^{-(\alpha^2 + \beta^2)^{1/2}}. \end{aligned} \quad (C-9)$$

APPENDIX C

Thus, substituting equations (C-7) to (C-9) into equation (C-5), we are left with the z-integral, which is an integral of an exponential in z multiplied by a polynomial in z. The result is

$$G(s - s_c, \alpha, p, q') = 4\alpha^3 \left\{ \frac{1}{8(R - \gamma)^4} [4(R - \gamma)^3 A + 2\alpha(R - \gamma)^2 B + 2\alpha^2(R - \gamma)C + 3\alpha^3 D] + \frac{s - s_c}{4(R - \gamma)^3} [2\alpha(R - \gamma)^2 B + 2\alpha^2(R - \gamma)C + 3\alpha^3 D] \right. \\ \left. + \frac{(s - s_c)^2}{4(R - \gamma)^2} [2\alpha^2(R - \gamma)C + 3\alpha^3 D] + \frac{1}{2} \frac{\alpha^3 D}{R - \gamma} (s - s_c)^3 \right\} e^{2(R - \gamma)(s_c - s)}, \quad (C-10)$$

where

$$\gamma = \pi \left(\frac{p^2}{a^2} + \frac{q'^2}{b^2} \right)^{\frac{1}{2}},$$

$$R = (\gamma^2 + \alpha^2)^{\frac{1}{2}}$$

$$A = \frac{\alpha}{2R^3} - \frac{21\alpha^3}{16R^5} + \frac{15\alpha^5}{16R^7},$$

$$B = \frac{1}{R^2} - \frac{21\alpha^2}{8R^4} + \frac{15\alpha^4}{8R^6},$$

$$C = \frac{7\alpha}{4R^3} + \frac{3\alpha^3}{2R^5},$$

$$D = \frac{\alpha^2}{2R^4}. \quad (C-11)$$

We may use the above to calculate the energy shifts. Defining

$$H(s - s_c, \alpha, p, q') \equiv [2 - G(s - s_c, \alpha, p, q')] / \quad (C-12)$$

$$\left\{ 2 - e^{-2\alpha(s-s_c)} \left[1 + \frac{3}{2} \alpha (s - s_c) + \alpha^2 (s - s_c)^2 + \alpha^3 (s - s_c)^3 \right] \right\},$$

we have for the point-charge potential shift, ΔE_p ,

$$\Delta E_p = - \frac{Qq^2}{ab} \sum_{i,p,q'=-\infty}^{\infty} \left(\frac{p^2}{a^2} + \frac{q'^2}{b^2} \right)^{-\frac{1}{2}} H(s - s_c, \alpha, p, q') \quad (C-13)$$

$$\cdot \exp \left\{ -2\pi i \left[\frac{p(x_0 + x_i)}{a} + \frac{q'(y_0 + y_i)}{b} \right] - 2\pi |z| \left(\frac{p^2}{a^2} + \frac{q'^2}{b^2} \right)^{\frac{1}{2}} \right\},$$

and for the surface-state potential shift, ΔE_s ,

$$\begin{aligned} \Delta E_s = & - \frac{q^2}{ab} \sum_{i,\ell,m,p,q'} (2\pi)^\ell q_{\ell m} \left(\frac{p^2}{a^2} + \frac{q'^2}{b^2} \right)^{\frac{\ell-|m|-1}{2}} H(s - s_c, \alpha, p, q') \\ & \cdot \exp \left\{ -2\pi i \left[\frac{p(x_0 + x_i)}{a} + \frac{q'(y_0 + y_i)}{b} \right] - 2\pi |z| \left(\frac{p^2}{a^2} + \frac{q'^2}{b^2} \right)^{\frac{1}{2}} \right\} \\ & \cdot [(\ell - m)(\ell + m)]^{\frac{1}{2}} \begin{cases} (-1)^m \left(\frac{q'}{b} - \frac{ip}{a} \right)^m, & m \geq 0, \\ \left(\frac{q'}{b} + \frac{ip}{a} \right)^{|m|}, & m < 0. \end{cases} \end{aligned} \quad (C-14)$$

SYMBOLS

a, b	lattice constants
J_0	Bessel function of zero order
p	momentum operator
q	electronic charge
Q	charge on lattice ion
s	distance of nucleus from surface
s_c	cutoff distance
x, y, z	coordinates of ad-atom electron relative to nucleus
x_i, y_i	coordinates of lattice ions in unit cell relative to origin
x_o, y_o	coordinates of nucleus of ad-atom relative to origin
ΔE_p	point-charge potential shift
ΔE_s	surface-state potential shift
ϕ	potential

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